

Colloid-borne uranium and other heavy metals in the water of a mine drainage gallery

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Summary. The water of a mine drainage gallery was investigated for its contents of colloid-borne heavy metals with emphasis on uranium. About 1 mg/L of colloid particles of 100 to 300 nm were found. They consist of a matrix of Fe and Al oxyhydroxides and are formed when anoxic slightly acidic shaft waters mix with oxic near-neutral gallery water. The colloid particles bear toxic trace elements such as As, Pb, and Cu. Almost 100% of the As and Pb and about 70% of the Cu contained in the water are colloid-borne. Carbonato complexes prevent the uranyl from being adsorbed on the colloids in the unaltered gallery water. Acidification destroys these complexes: up to 50% of the uranium is attached to the colloids in the slightly acidic pH region. Further acidification converts the uranyl again to a 'non-colloidal' form.

1. Introduction

The chemical composition of mine drainage waters, the nature of solid precipitates developing in such waters, and the relationships between the solutions and the precipitates have repeatedly been studied [1–3]. Iron and aluminum oxyhydroxides are the most common precipitates sedimented from mine drainage. The formation of secondary minerals in the form of relatively stable colloids in mine drainage waters has been considered much less frequently. Colloids from mining waters may influence the transport behavior of trace element contaminants within the mine drainage systems and subsequently in rivers, river seepage waters, waterworks, and the estuaries of rivers. The assessment of the colloid inventories in the mining waters and the physico-chemical characterization of the colloidal particles should be the first step when assessing the colloidal transport of contaminants from mines to the farther environment. The water of the drainage gallery Rothschnberger Stolln (Freiberg, Germany, mining area) is a typical mining water of high mineral contents. It contains toxic trace elements such as As, Pb, Cd, Zn, and Cu. The particles of the gallery water are characterized, the colloid-borne heavy metals are identified, and the chemical state of the colloid-borne heavy metals is discussed. Emphasis is placed on the behavior of uranium.

2. Experimental

2.1 Site description

The abandoned zinc-lead-silver mine at Freiberg, Saxony, has a depth of about 700 m and is now flooded. Its water level at a depth of 227 meters is established by the location of the main drainage gallery named Rothschnberger Stolln. In the southern shafts of the mine, surface waters sink to the floors. They move through galleries and rise in a northern shaft toward the main drainage gallery. The rising water is slightly acidic, highly mineralized and poor in oxygen. After the access of the shaft water to the drainage gallery, the water becomes oxic and increases in pH. The mouth of the gallery, where the water enters a tributary of the river Elbe, is located 13.5 km from the shaft. At the mouth, the water is almost saturated with air and the chemical conditions should approach a steady state. The water flows through the gallery at about 500 liters per second.

2.2 Sampling and sample treatment

The samples were taken at the mouth of the gallery by scooping from the turbulently streaming water. They were stored and transported in polyethylene vessels cleaned with 1 M HNO₃ and rinsed with Milli-Q water (Millipore, Eschborn, Germany). The colloid investigations began about 3 h after sampling.

2.3 Analytical methods

The samples were investigated with the following techniques: photon correlation spectroscopy, PCS (BI-90, Brookhaven Instruments, Holtsville, USA), filtration (Nuclepore filters, Costar, Cambridge, USA), ultrafiltration (Amicon, Beverly, USA), centrifugation (Kontron T 124, Kontron GmbH, Neufahrn, Germany), scanning electron microscopy, SEM (Zeiss, Oberkochen, Germany). The centrifugates, filtrates and filter cakes were analyzed by ion chromatography (Jasco, Großumstadt, Germany), inductively coupled plasma mass spectrometry, ICP-MS (Elan 5000, Perkin Elmer, Überlingen, Germany) and/or atomic absorption spectroscopy, AAS (AAS 4100, Perkin Elmer, Überlingen, Germany).

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3. Results and discussion

3.1 Unaltered gallery water

The salt content of the water (pH 7.2) is dominated by sulfates, carbonates, and chlorides of calcium, sodium, and magnesium. Table 1 gives selected cation and anion concentrations. PCS measurements revealed the presence of colloidal particles of 100 to 300 nm. Fig. 1 shows the decrease of the scattered light intensity and the concentration of several chemical elements after the centrifugation with increasing centrifugal acceleration and centrifugation times, and Fig. 2 gives the same for a filtration experiment with decreasing filter pore sizes (geometric pore size of the 3-kD ultrafilter: about 1.3 nm). The behavior of the scattered light intensity indicates the disappearance of particulate matter by the centrifugation and the filtration operations. The chemical elements follow two different patterns. Elements whose concentration was diminished by the centrifugations and filtrations are regarded as particulate (colloidal). Elements not influenced by these operations were taken as truly dissolved (if the possible trace of particles between ion size and 1.3 nm is neglected). Most of the 25 chemical elements that

Table 1. Results of ICP/MS, AAS and Ion Chromatography on the Unfiltered Mine Drainage Gallery Water. Values are given with standard deviations.

Component	Concentration [Mol/L]
Fe	$1.5(0.2) \times 10^{-5}$
Al	$1.1(0.2) \times 10^{-5}$
Pb	$1.2(0.3) \times 10^{-7}$
Na	$2.2(0.2) \times 10^{-3}$
As	$2.0(0.3) \times 10^{-7}$
Cu	$6.0(1.9) \times 10^{-7}$
Zn	$7.4(0.7) \times 10^{-5}$
Mg	$1.1(0.1) \times 10^{-3}$
Ca	$2.7(0.1) \times 10^{-3}$
Si	$1.9(0.5) \times 10^{-4}$
Cd	$2.6(0.3) \times 10^{-7}$
U	$7.0(0.4) \times 10^{-9}$
Mn	$4.2(0.3) \times 10^{-5}$
Sulfate	$3.65(0.23) \times 10^{-3}$
Carbonate	$1.75(0.31) \times 10^{-3}$

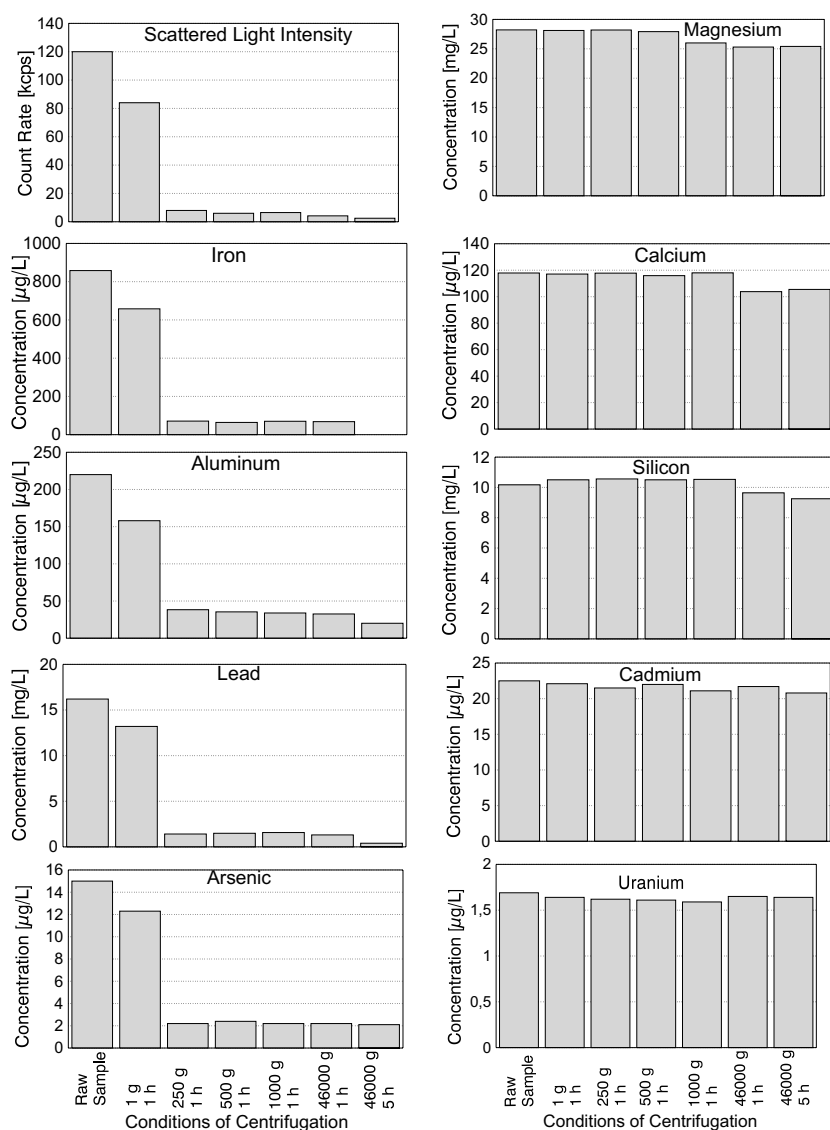


Fig. 1. Scattered light intensity (photomultiplier count rate of the PCS device; scattering angle 90°) and concentration of some typical elements after the centrifugation at varying centrifugal acceleration and centrifugation time.

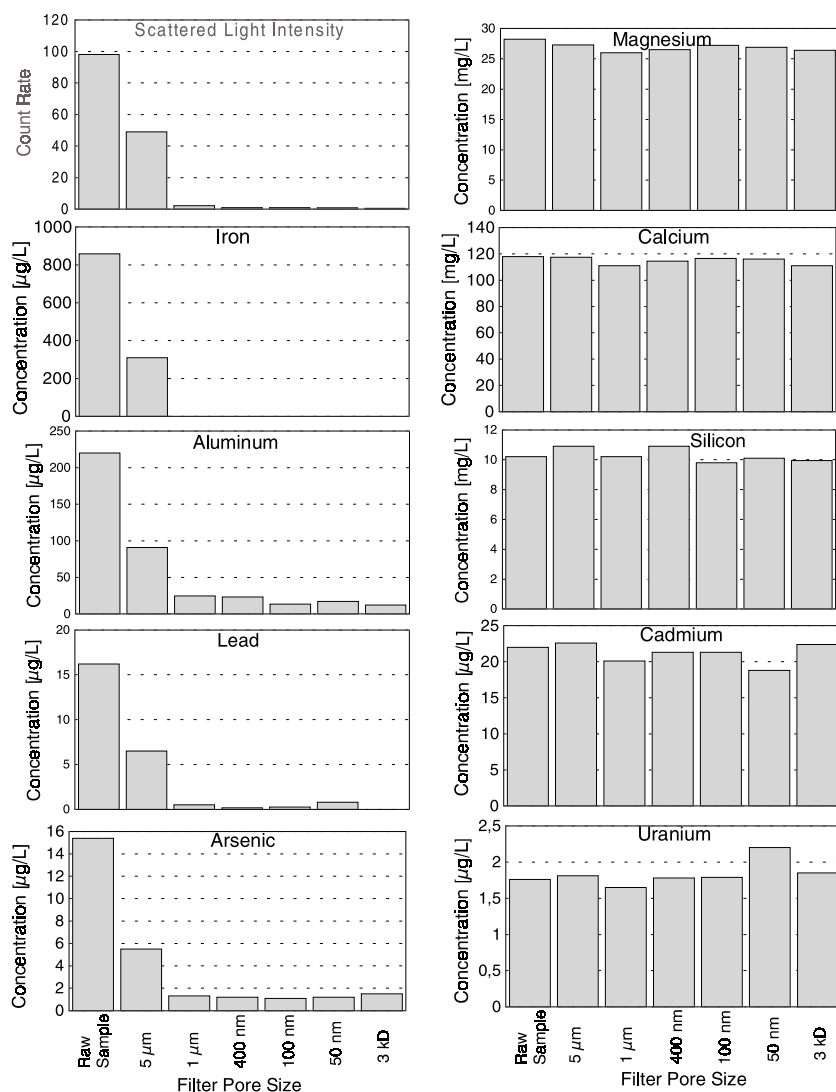


Fig. 2. Scattered light intensity (photomultiplier count rate of the PCS device; scattering angle 90°) and concentration of some typical elements after the filtration through filters of varying pore size.

we analyzed were truly dissolved according to this differentiation. Fe, Al, As, Pb, and Cu showed colloidal behavior. From the ICP-MS/AAS analyses on the centrifugates, filtrates, and filter cakes we concluded that the water of the gallery contains about 1 mg/L of colloidal particles and that the matrix of the particles consists of Fe and Al compounds. This colloid matrix carries trace elements such as As, Pb, and Cu. Cadmium, uranium, and a number of other contaminants exhibit 'non-colloidal' behavior. Fig. 3 shows an SEM micrograph of the deposits on a 5- μm filter confirming the existence of the particles in the 100- to 300-nm size range found by PCS. The filter cake was washed three times with 20 mL of Milli-Q water, dried, and coated with gold. We repeated this SEM visualization experiment performing ten-fold washing of the filter cake before drying and coating it to make sure that the depicted particles are real and not an artifact from salt crystallization (micrograph not given here). The particles are detectable also after this rigorous rinsing which underlines their insoluble nature. Salt crystallization can also be ruled out because EDX spectra indicate Fe, Al, As, and Pb as the major particle constituents with only occasional traces of Ca, Na, Zn, or Si. Obviously, the 5- μm filters have retained significant amounts of the 100- to 300-nm particles although their size is far below the filter pore size.

Note that filtration is not a 'sieving' process like sieving of powders in air but a process also governed by particle aggregation in the fluid-to-membrane interface layer and by adsorption of particles onto the membrane [4, 5]. The small particles are arranged on the filter as aggregates of several μm diameter (Fig. 4a). Because of the known susceptibility of filtration to artefacts, it can not be decided from the SEM images alone whether or not these aggregates exist also in solution. However, it follows from the in-situ measurements by PCS that the 100- to 300-nm particles move freely in the solution and that the aggregates are formed on the filter membrane during filtration ('self-coagulation', cf. [4]).

Our methods of direct particle sizing, SEM and PCS, have lower particle size detection limits of about 50 nm under the given conditions. For SEM, 50 nm is the limit of resolution. For PCS, problems arise from the scattered light intensity which is strongly decreasing with particle size if the particles are smaller than 50 nm (region of Rayleigh scattering). Thus the question may be asked if we have overlooked a significant colloid population of the size range below 50 nm. However, this can be ruled out because of the centrifugation and the filtration results (Figs. 1 and 2). A centrifugal acceleration larger than 5000 g (centrifugation time 1 h) would be necessary under our centrifugal condi-

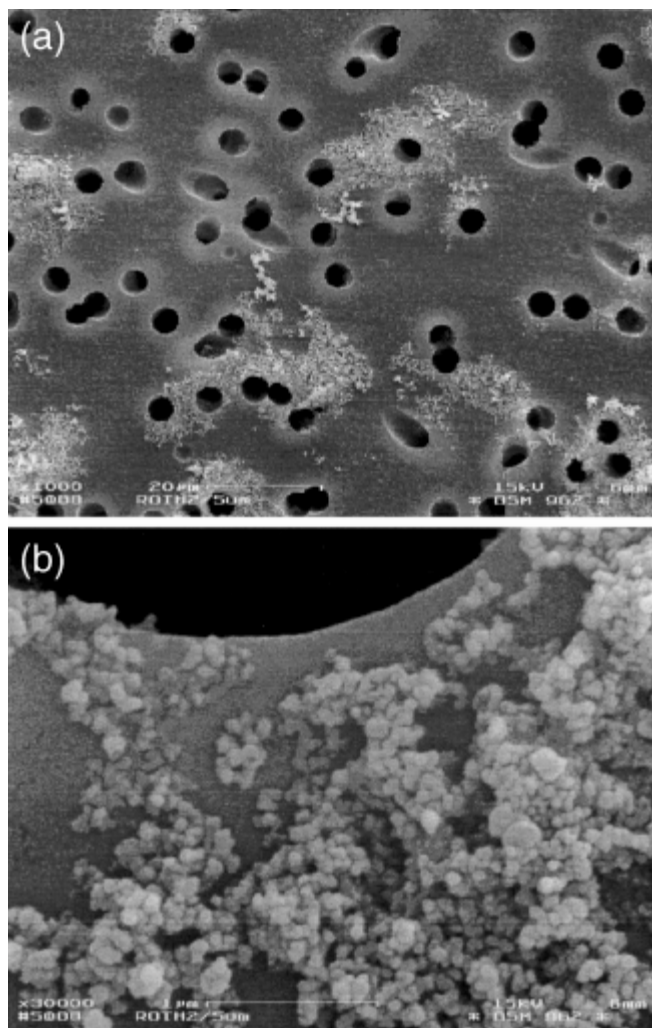


Fig. 3. SEM micrographs of particle agglomerates on a 5- μm Nucleopore filter. The filter cake was washed three times, dried, and coated with gold. (a) Magnification 1 : 1000. (b) Magnification 1 : 30 000.

tions to remove Fe or Al oxyhydroxide particles smaller than 50 nm. As Fig. 1 shows, almost all the ‘colloidal’ Fe, Al, Pb, and As has been removed at significantly lower centrifugal forces. The filtration experiment (Fig. 2) shows that stable Al, Pb, As (and obviously Fe the value of which dropped below detection limit) concentrations are reached by the 1- μm filtration with almost no further decrease for the smaller filter pore sizes (the high filtration efficiency of the 1- μm filters for 100- to 300-nm particles is also attributable to ‘self-coagulation’ and adsorption). Only the existence of a tiny trace of particles smaller than 1.3 nm can not be completely excluded. The predominance of iron oxyhydroxide particles of the 50–400 nm size range (composed of very small units of 1 to 2 nm) is typical of natural waters that are near steady state conditions [6–8]. The relative stability of this particle size range is attributable to an ‘aggregation bottle neck’ [6], i.e., to coagulation kinetics. Whereas particles below 50 nm possess a very fast coagulation kinetics [9] and produce particles of the stable size range very quickly, particles larger than 400 nm are formed very slowly because the ‘stable’ particles have a slow coagulation kinetics (the latter being due to their low diffusion coefficient).

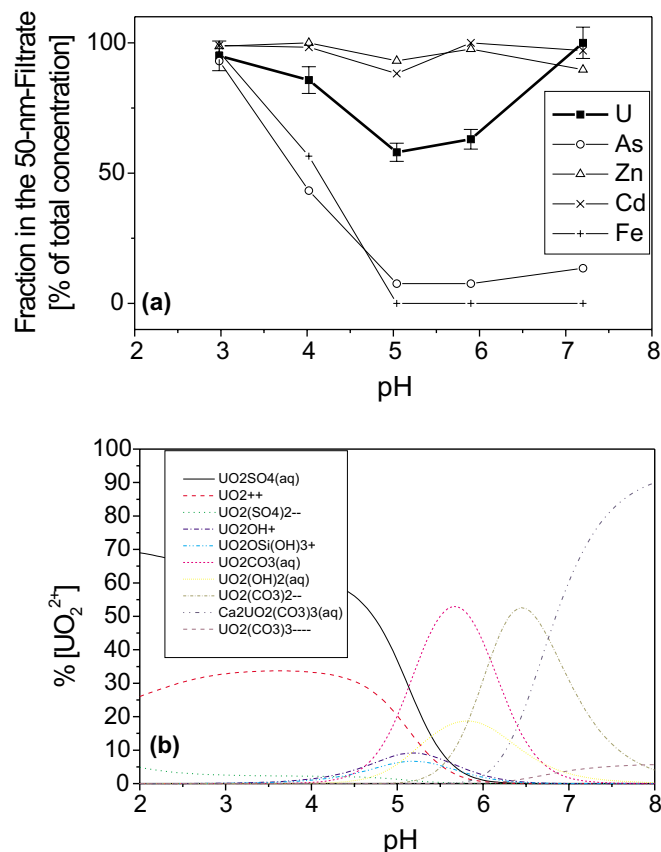


Fig. 4. Heavy metal behavior in the gallery water on acidification: (a) Influence of pH on the colloid-borne fraction of several heavy metals. Error bars: 2σ confidence intervals of the measured uranium concentration. (b) Uranyl speciation in water of the mining gallery for varying pH values. Computed with EQ3/6, based on the NEA TDDb [19] with the addition of the $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3(\text{aq})$ complex [20].

The iron and aluminum oxyhydroxide particles probably originate in the area where the anoxic and slightly acidic shaft water from the depth mixes with the oxidic, near-neutral gallery water. Here, the ferrous iron is oxidized and the Fe(III) and Al oxyhydroxides are precipitated. Thus the entrance of the shaft water to the drainage gallery forms a large ‘geochemical colloid generator’.

We performed thermodynamic calculations with the geochemical computer code EQ3/6 [10] for the elements found in the unfiltered sample (Table 1) to identify the chemical compounds that are oversaturated, i.e., that are potential colloid-forming compounds. Iron and aluminum oxyhydroxides were predicted to form precipitates at the given conditions. These are the matrix compounds of the experimentally determined colloids. Moreover, cerussite (PbCO_3) is predicted to precipitate. The calculations did not predict the experimental findings for As and Cu. No oversaturation was calculated for these elements whereas they showed ‘colloidal behavior’ in the experiments. It is possible that (i) the compounds of these elements are really not oversaturated and their ‘insolubility’ is exclusively attributable to adsorption onto the colloid matrix, or (ii) that the calculations are insufficient due to an incomplete thermodynamic data base for As and Cu. The chemical binding of arsenate to iron(III) oxyhydroxides is currently being discussed [11–15]. X-ray absorp-

tion fine structure (XAFS) spectroscopy shows that the formation of iron arsenate mineral phases such as scorodite ($\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$) or kankite ($\text{FeAsO}_4 \cdot 3.5\text{H}_2\text{O}$) is very unlikely in the near-neutral pH region [11–14] which is in accordance with the results of previous investigations on the stability of iron arsenate for $\text{pH} > 2$ via solubility measurements [16]. Normally, the arsenic is bound to the iron oxyhydroxides by adsorption in this pH region. The high sorption affinity and sorption capacity is attributed to the formation of inner-sphere surface complexes. However, the nature of these complexes (mono- or bidentate, mono- or binuclear) is still disputed [11–13]. Only in natural aquatic iron-arsenic precipitates that have undergone long aging times, the formation of arsenate minerals seems to occur [15]. In the light of the literature, the most probable type of bonding of the arsenic to the Fe and Al oxyhydroxide colloid particles in the Rothschröberger Stolln gallery is the formation of surface complexes. Thus the EQ3/6 results might be quite reasonable for As (case (i)). However, only further experimental work can really provide insight into the bonding of the heavy metals to the colloidal particles. XAFS measurements to elucidate the attachment of As, Pb, and Cu onto the particles of the Rothschröberger Stolln water are under way.

3.2 Acidified samples

Uranium showed strictly ‘non-colloidal’ behavior. This was somewhat surprising because uranium normally has a pronounced tendency to adsorb onto ferrihydrite [17]. We tested the behavior of uranium and other metals in the gallery water at varying pH values by acidifying the water step by step with nitric acid. This experiment simulated the behavior of the trace elements in acidic mining waters.

We investigated the pH-behavior of 25 elements by filtration and ICP-MS/AAS. Fig. 4a shows five examples. Given are the fractions of the elements that passed through a 50-nm Nuclepore filter as a function of pH. Most of the elements had a ‘non colloidal’ behavior like Cd and Zn in the pH range from 7.2 to 3. For the ‘colloidal’ elements, as represented by Fe and As, the colloidal fraction decreases with decreasing pH. This is due to both the disappearance of the colloidal particles by dissolution of the colloid matrix and the decrease of the adsorption affinity of the trace elements in the more acidic pH region.

Uranium has another behavior than the other metal ions. The fraction of the uranium that is not removable by a 50-nm filter has a minimum around pH 5 (Fig. 4a). We explain this minimum by the complexation behavior of the dissolved uranium and by the surface complexation phenomena occurring at the colloid-solution interface. Figure 4b shows the calculated uranyl speciation in the gallery water as a function of pH. As can be seen from this figure, the uranyl complexes prevailing at the pH of the original water (pH 7.2) are $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3(\text{aq})$ and $\text{UO}_2(\text{CO}_3)_2^-$. Obviously, these complexes do not significantly sorb onto the iron oxyhydroxide colloid particles, whereas in the pH region 5 to 6 the then prevailing species $\text{UO}_2\text{CO}_3(\text{aq})$ does sorb [17], resulting in a strong uranyl adsorption in that pH range. Such a difference in the adsorption behavior of the uranyl carbonate complexes of a ligand number of one compared to those of higher ligand numbers may be caused by steric effects and

by differences in the shielding of the complexed uranyl from the Fe/Al oxyhydroxide surfaces.

Calculations with MINTEQA2 [18] to model the surface complexation processes at the colloid-solution interface and to evaluate the fractions of the individual complexes adsorbed to the colloid particles are in progress. A very first result of these calculations is that an alternative explanation of the adsorption behavior of the uranyl on the Fe/Al oxyhydroxide particles can be ruled out: According to MINTEQA2, the low U adsorption at pH values above 7 is not caused by a competition between uranyl adsorption and carbonate adsorption which was a first hypothesis (note that the carbonate concentration in the gallery water is about 10^6 times that of the uranyl concentration).

If the pH is decreased below 4, the colloidal Fe/Al oxyhydroxide particles start to dissolve. Therefore, the uranyl species lose their ‘colloidal’ properties again in this region.

4. Conclusion

When anoxic waters rising from the depths of the mine mix with oxic gallery water, Fe(III) and Al oxyhydroxide colloids precipitate. These colloids carry trace elements such as As, Pb, and Cu. Almost 100% of the water’s As and Pb and about 70% of the Cu are colloid-borne. At the mouth of the drainage gallery, the colloid concentration is about 1 mg/L with a particle size of 100 to 300 nm. Both precipitation (lead) and surface inner sphere complexation (arsenic) seem to play a role for the binding of the trace heavy metals to the particles. Uranium behaves differently from the other metal ions. Uranyl carbonate complexes of ligand numbers > 1 prevent the uranyl from being adsorbed to the colloids in the unaltered gallery water. Acidification destroys these complexes: up to 50 mass percent of the uranyl is attached to the colloids in the slightly acidic pH region. Further acidification, however, converts the uranyl again to a ‘non-colloidal’ form.

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